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Chemical Kinetic Modeling of Hydrogen Combustion Limits

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Abstract

A detailed chemical kinetic model is used to explore the flammability and detonability of hydrogen mixtures. In the case of flammability, a detailed chemical kinetic mechanism for hydrogen is coupled to the CHEMKIN Premix code to compute premixed, laminar flame speeds. The detailed chemical kinetic model reproduces flame speeds in the literature over a range of equivalence ratios, pressures and reactant temperatures. A series of calculation were performed to assess the key parameters determining the flammability of hydrogen mixtures. Increased reactant temperature was found to greatly increase the flame speed and the flammability of the mixture. The effect of added diluents was assessed. Addition of water and carbon dioxide were found to reduce the flame speed and thus the flammability of a hydrogen mixture approximately equally well and much more than the addition of nitrogen.

The detailed chemical kinetic model was used to explore the detonability of hydrogen mixtures. A Zeldovich-von Neumann-Doring (ZND) detonation model coupled with detailed chemical kinetics was used to model the detonation. The effectiveness on different diluents was assessed in reducing the detonability of a hydrogen mixture. Carbon dioxide was found to be most effective in reducing the detonability followed by water and nitrogen.

The chemical action of chemical inhibitors on reducing the flammability of hydrogen mixtures is discussed. Bromine and organophosphorus inhibitors act through

catalytic cycles that recombine H and OH radicals in the flame. The reduction in H and OH radicals reduces chain branching in the flame through the $H + O_2 = OH + O$ chain branching reaction. The reduction in chain branching and radical production reduces the flame speed and thus the flammability of the hydrogen mixture.

Introduction

Detailed chemical kinetic models can be very helpful is assessing the limits of flammability and detonability of fuel-air mixtures [2-4]. They can be used to estimate flammability and detonability limits at conditions of pressure, temperature and reactant concentration where no measurements are available. When considering the consequences of an accidental release of hydrogen, a broad range of conditions need to be considered. Detailed chemical kinetic models can also be used to assess to potential of diluents and chemical inhibitors to reduce the flammability and detonability of fuel-air mixtures [5-7]. The reactions, rate constants and species involved with the inhibition process need to be added to the reaction mechanism to address the chemical effect of inhibitors.

Recently, a chemical kinetic mechanism for hydrogen oxidation has been improved and updated [8]. The mechanism includes more accurate thermodynamic properties for species. The rate constant estimations are improved based on recent reaction rate measurements in the literature. This development allows more accurate estimations of flammability and detonability limits for hydrogen mixtures.

Technical approach

Our technical approach is to use a detailed chemical kinetic mechanism for hydrogen oxidation in conjunction with numerical models that solve the equations of mass, momentum, energy and species transport to examine combustion limits. In this work, we first validate the detailed chemical kinetic model for hydrogen mixtures at different pressures, temperatures and equivalence ratios. Then we use the model to predict the flammability for a test mixture and to evaluate the effectiveness of different diluents. Next, we examine the detonability of a test mixture and the effectiveness of various diluents in reducing detonability. Finally, we examine how inhibitors work to reduce flammability.

Chemical Kinetic Model

The detailed chemical kinetic mechanism of O'Conaire, Curran, Simmie, Pitz and Westbrook [8] was used to simulate flame speeds for hydrogen mixtures. The CHEMKIN 4.1.1 software package for chemical reacting flows was used to solve the conservation equations of mass, momentum, energy and species [9].

Flammability of Hydrogen Mixtures

In order to predict accurate flammability limits, it is important to predict accurate flame speeds over a wide range of conditions. Fig. 1 shows the detailed chemical kinetic models predictions over a wide range of equivalence ratios for one atmosphere and an unburned reactant temperature of 298 K. In the calculations, 400-500 computational zones were used to accurately resolve the flame. Multi-component and thermal diffusion were included in the transport model to accurately simulate species transport. The

experimental data shown in Fig. 1 were obtained from a large number of experimental studies on hydrogen-air mixtures [10-18]. The detailed chemical kinetic model well predicts the laminar flame speeds over a wide range of equivalence ratios. It is particularly important to predict the laminar flame speed near the flammability limit. In Fig. 2, the flame speeds are expanded at low equivalence ratio to get a closer view near the lean flammability limit. It is clear that the detailed chemical kinetic model does a good job of simulating the laminar flame speed for lean mixtures near the lean flammability limit.

In hydrogen storage systems, the pressure of hydrogen will exceed one atmosphere. In Fig. 3, the behavior of the detailed chemical model is given at an elevated pressure of 5 bar. The experimental flames speeds were recently measured by Bradley et al. [1]. The detailed chemical kinetic model does a good job of simulating these experimental flame speeds at evaluated pressure.

In the next series of calculations, the flammability of a test mixture containing hydrogen was examined to look at how reactant temperature affects the flammability. Also, different diluents were examined to see the effectiveness of diluents in reducing the flammability of the test mixture.

The test mixture examined is one that was used in a previous study [19] and which proved useful in examining flammability issues for hydrogen. The composition of the mixture is shown in Table 1.

In the computational model, a flame speed of 5 cm/sec is used as a criterion for determining if a mixture is flammable. If the computed flame speed is below 5 cm/sec, the reactant mixture is predicted to be not flammable. If the computed flame speed is

above 5 cm/sec, the reactant mixture is predicted to be flammable. Although the value of the limit is somewhat arbitrary, this criterion has been successful in predicting the flammability of fuel-air mixtures [2].

The flammability of the test mixture as the unburned temperature is increased is explored in Fig. 4. The test mixture is not flammable for temperatures below about 400K. If the test mixture is raised above 400K, the mixture becomes flammable. The flame speed of the mixture rises rapidly for temperatures above 500K. The results show that reactant temperature is an important parameter affecting flammability of hydrogen mixtures.

In the next series of calculations, the effectiveness of different diluents in reducing the flammability of the test hydrogen mixture was examined. Three diluents were examined: N_2, H_2O and CO_2. In order to increase the flammability of the test mixture so that the effectiveness different diluents could be assessed, an air leak was assumed so that the test mixture had a computed flame speed of 40 cm/sec. Nitrogen, water and carbon dioxide were added to the test hydrogen mixture, in turn, to assess their effectiveness in reducing the flammability of the mixture below the flammability limit. First, nitrogen was added as a diluent. The computed flame speed as reduced from 40 cm/sec with no added N_2 to the critical limit of 5 cm/sec with 32% N_2 added (Fig. 5). As noted above for mixtures with computed flame speeds of 5 cm/sec or lower, the mixture is predicted to be not flammable. Next, H_2O and CO_2 were computationally tested, in turn. These diluents behaved very similarly. With added H_2O or CO_2, the computed flames speeds were reduced from 40 cm/sec with no diluent to the critical limit of 5 cm/sec with about 22 % H_2O or CO_2 (Fig. 5). Thus, water and carbon dioxide are found

to be about equally effective in reducing the flammability of the test hydrogen mixture. Nitrogen is found to be significantly less effective than water or carbon dioxide in reducing flammability.

Detonability of Hydrogen Mixtures

In the next section of this study, we examine the detonability of hydrogen mixtures. In order to understand our approach for computing detonability, we need to review how detonation limits are experimentally determined and how the experimental limits are related to the computational model.

For a cylindrical tube, the characteristic cell size of detonation is a useful concept to determine if a mixture is detonable or not detonable in the tube. When a detonation propagates down the inside of a tube, it inscribes a cellular structure on the inside wall of the tube when the wall has been covered with a sooted foil (Fig. 6) [20]. The average width of the cells is dependent on the initial composition, temperature and pressure of the reactant mixture in the tube. If the circumference of the tube is reduced below the characteristic cell size of the mixture, that mixture will not be able to maintain a detonation in the tube [21]. Thus the cell size of the mixture can be used to determine if a reactant mixture is detonable or not in a given size tube. If hydrogen mixtures are stored in a cylindrical tank, the cell size of the reactant mixture can be used to predict if the mixture is detonable when stored in the tank.

To use the concept of cell size to predict the detonability of a mixture in a tube, a numerical model needs to be able to compute the cell size of a reactive mixture. Westbrook and co-workers [3, 22] correlated the cell sizes of fuel-air mixtures with the

computed induction length from a Zeldovich-von Neumann-Doring (ZND) detonation model. For hydrogen-air mixtures, a proportionality constant of 52 shows good agreement:

$$\lambda = 52\,\Delta \qquad (1)$$

where λ is the cell width of the hydrogen mixture and Δ is the induction length calculated by the ZND model. Next we need to describe the ZND model and how the induction length, Δ, is computed.

The Zeldovich-von Neumann-Doring (ZND) model simulates a detonation as a shock wave traveling at the Chapman-Jouguet (CJ) velocity. The shock wave compresses and heats the hydrogen mixture which then begins to react. The reaction region behind the shock wave consists of a relatively long induction period where the pressure and temperature behind the shock wave is relatively constant, followed by a rapid increase in temperature and pressure at the end of the induction period (Fig. 7).

In a calculation, the CJ conditions are first computed to obtain the CJ detonation velocity. Then, the conditions behind a shock wave traveling at the CJ velocity are computed including the pressure, temperature and particle velocity behind the shock. Finally, a detailed chemical kinetics calculation is performed at the conditions behind the shock wave to get the induction time. The induction time is the characteristic time that the mixture takes to ignite at the conditions behind the shock wave (Fig. 7). An induction length, Δ, can be calculated from the induction time, τ, using the relation

$$\Delta = \tau(D_{CJ} - v_1) \qquad (2)$$

where D_{CJ} is the detonation velocity and v_1 is the particle velocity behind the shock. Using Equation 1, the cell size of a mixture can be calculated from the computed induction length.

Following the procedure outlined above, we assessed the effectiveness of different diluents in reducing the detonability of the test hydrogen mixture. Again, the diluents were nitrogen, water and carbon dioxide. Since the test mixture is not very detonable, we assumed that there is an air leak so that the oxygen mole fraction in the mixture is increased to 10 % to increase the detonability of the mixture. With this mixture, the effectiveness of the different diluents in reducing detonability of the mixture was assessed. As discussed above, the detonability of the mixture in a tube depends on the circumference of the tube. If the characteristic cell size of the mixture, λ, is greater than the circumference of the tube, πd, the mixture cannot sustain a detonation in that tube. Expressed as an equation, the criterion for a mixture to be not detonable in a tube is

$$\lambda > \pi d \qquad (3)$$

where d is the diameter of the tube. To perform an assessment for detonability, a tube diameter must be selected. As an example, we choose a 1.6 m diameter tube. This would be representative of a 1.6 m diameter cylinder vessel used to store a hydrogen mixture. Using Equations 1 and 3 above, a critical induction length, Δ_{CRIT} of 0.1 m can be obtained. If the reactant mixture has a computed induction length below 0.1 m, the mixture is predicted to be detonable in the cylindrical vessel. If the reaction mixture has a computed induction length above 0.1 m, the mixture is predicted not to be detonable. In Fig. 8, we use this method to assess the effectiveness of different diluents in reducing the detonability of the test mixture. In Fig. 8, the induction length of the baseline test

mixture with an air leak is below 0.007 m. This is below the critical induction length of 0.1 m. Therefore, the baseline mixture is detonable when stored in a 1.6 m diameter cylindrical vessel. Nitrogen, water and carbon dioxide are added, in turn, to the mixture until the hydrogen mixture is not detonable in the 1.6 m diameter vessel. As seen in Fig. 8, 26 % of nitrogen needs to be added to the mixture before the computed induction length of mixture is greater than 0.1 m and it is not detonable in the specified vessel. For H_2O, 17% diluent needs to be added to the mixture to make it not detonable. Finally for CO_2, 12% of this diluent needs to be added to make the hydrogen mixture not detonable. Based on these calculations, the effectiveness of these diluents in reducing the detonability of the hydrogen mixture is:

$CO_2 > H_2O > N_2$

These results indicate that carbon dioxide is the most effective diluent in reducing the detonability of the hydrogen mixture.

Chemical Inhibitors of Flammability and Detonability

Some suppressants act chemically to reduce flammability and detonability, rather than by dilution of the reactant mixture. These chemical suppressants include halogens, organophosphates and iron-containing compounds [23]. In the following discussion, we review how these chemical inhibitors act.

Halogen inhibitors such as CF_3Br and CH_3Br are effective in reducing the flame speeds and flammability of hydrogen mixtures [7]. These chemical inhibitors act by producing HBr and Br_2 in the flame. These species act through an inhibition sequence that leads to recombination of reactive H atoms to H_2 [7] (Fig. 9). The loss of H-atoms

inhibits the flame by reducing the rate of the main chain branching reaction in the flame that produces flame radicals:

$$H + O_2 = OH + O \qquad (4)$$

The rate of flame propagation is most sensitive to the rate of this main chain branching reaction [8]. Introduction of the bromine inhibitor slows the flame speed and reduces the flammability of the hydrogen mixture.

Another type of effective chemical inhibitor is an organophosphate. This class of inhibitors also acts to reduce hydrogen flame speed and flammability through a catalytic cycle [24] that reduces radicals in the flame. The catalytic cycle is shown in Fig. 10. Again, highly reactive flame radicals, H and OH, are combined to form a molecular product (in this case H_2O). This reduces the radical levels in the flame and reduces the production of radicals in the flame through the main chain branching reaction (Reaction 4 above). Since the flame speed depends greatly on the chain branching rate, the flame speed and the flammability of the mixture are reduced with the addition of organophosphorus compounds.

Summary

A detailed chemical kinetic model was used to assess the flammability and detonability of hydrogen mixtures. The detailed chemical kinetic model reproduced the flame speeds for hydrogen mixtures over a broad range of equivalence ratios and at elevated pressures and temperatures. The model was used to assess the effects of hydrogen mixture temperature and different diluents on flammability. Increased reactant temperature was found to increase the flame speed and flammability of the hydrogen

mixture. Water and carbon dioxide were found to be the most effective diluents in reducing the flammability of a hydrogen mixture. Nitrogen was found to be a much less effective diluent than water or carbon dioxide.

In another series of calculations, detonability of hydrogen mixtures was explored. The effectiveness of different diluents in reducing the detonability of a hydrogen mixture was assessed. Carbon dioxide was found to be the most effective diluent in reducing the detonability of a hydrogen mixture, followed by water and nitrogen.

Finally, the action of chemical inhibitors was discussed. Both bromine and organophosphorus inhibitors act by recombining flame radicals like H and OH in catalytic cycles. This loss of flame radicals slows the flame speed through the $H + O_2 = OH + O$ chain branching reaction. Therefore, adding these chemical inhibitors to hydrogen mixtures reduces the flammability of the mixture.

Acknowledgements

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Table 1: Test Hydrogen Mixture Composition

Species	Mole Fraction
H_2	17 %
CO	18 %
O_2	4 %
CO_2	1 %
H_2O	10 %
N_2	50 %

Figures

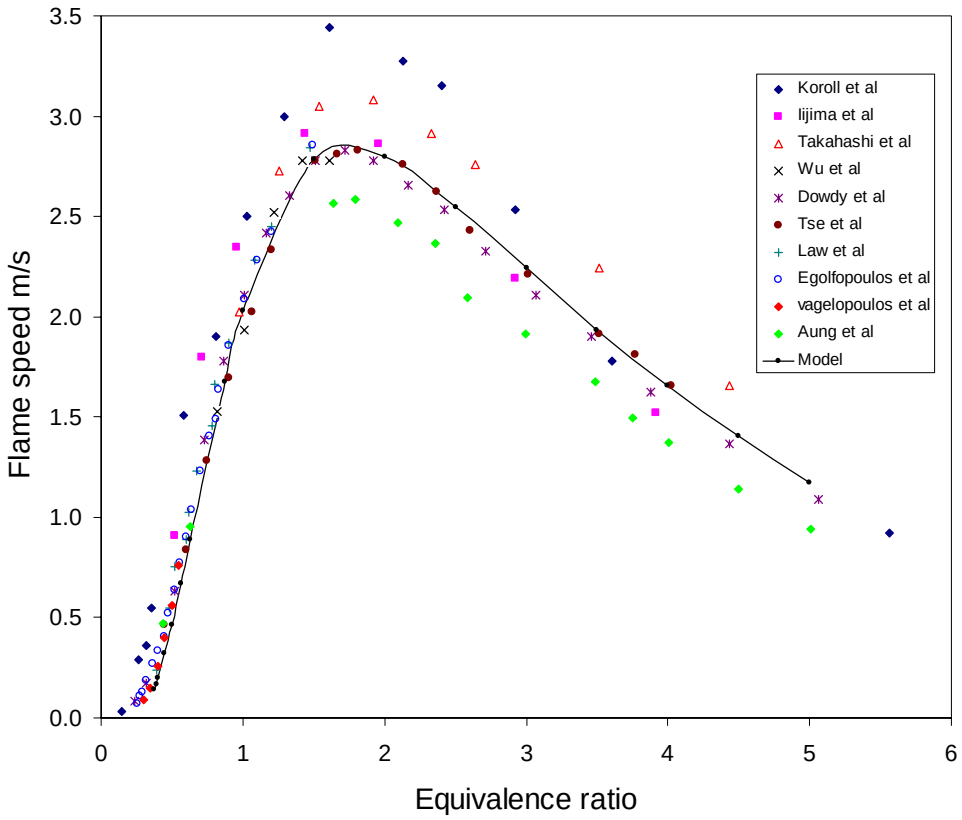

Figure 1: Computed and experimental [10-18] flame speeds over a wide range of equivalence ratios at a pressure of 1 atm and a reactant temperature of 298 K.

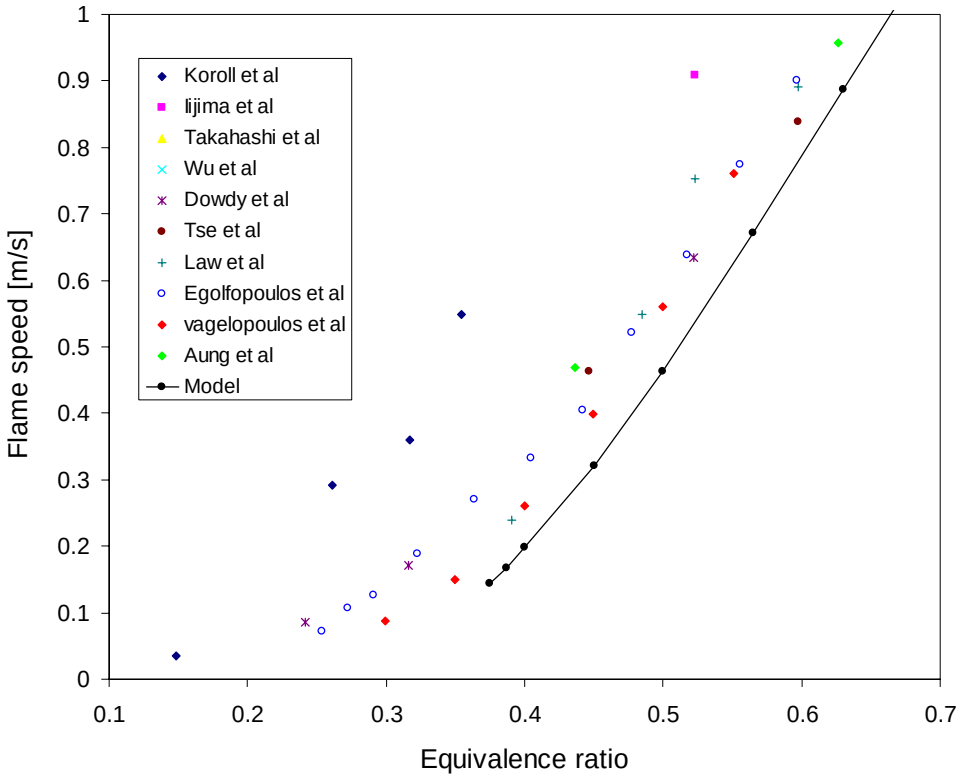

Figure 2: Computed and experimental [10-18] flame speeds near the lean flammability limit at a pressure of 1 atm and a reactant temperature of 298 K.

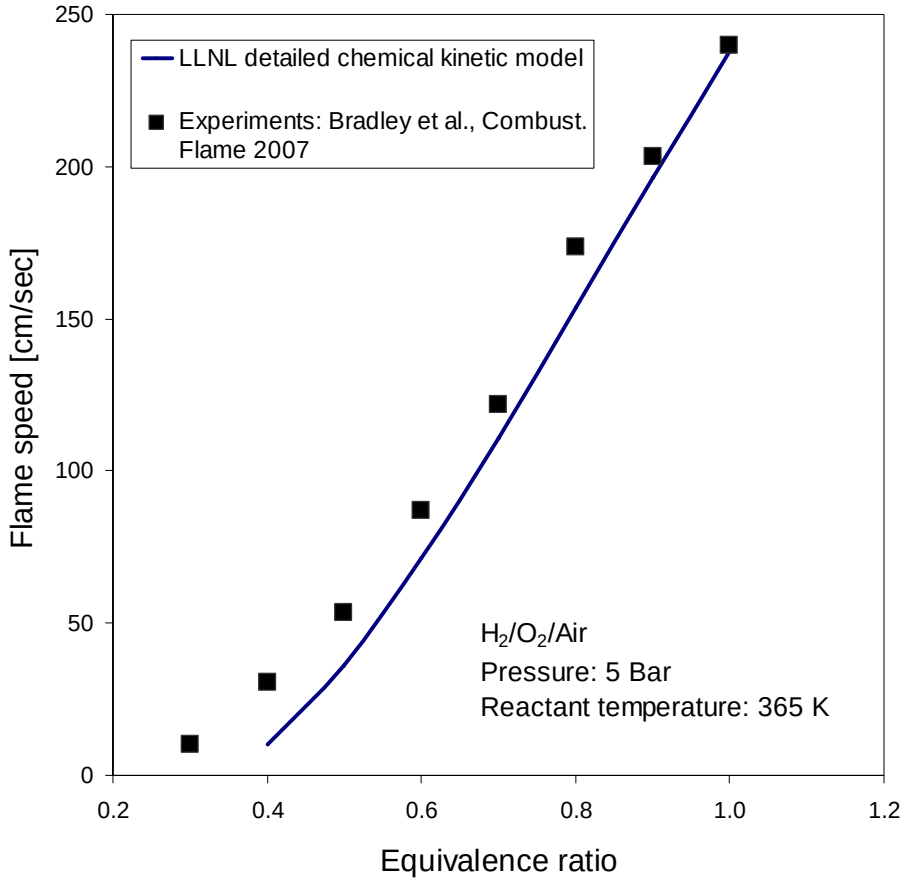

Figure 3: Computed and experimental [1] flame speeds near the lean flammability limit at a pressure of 5 bar and a reactant temperature of 365 K.

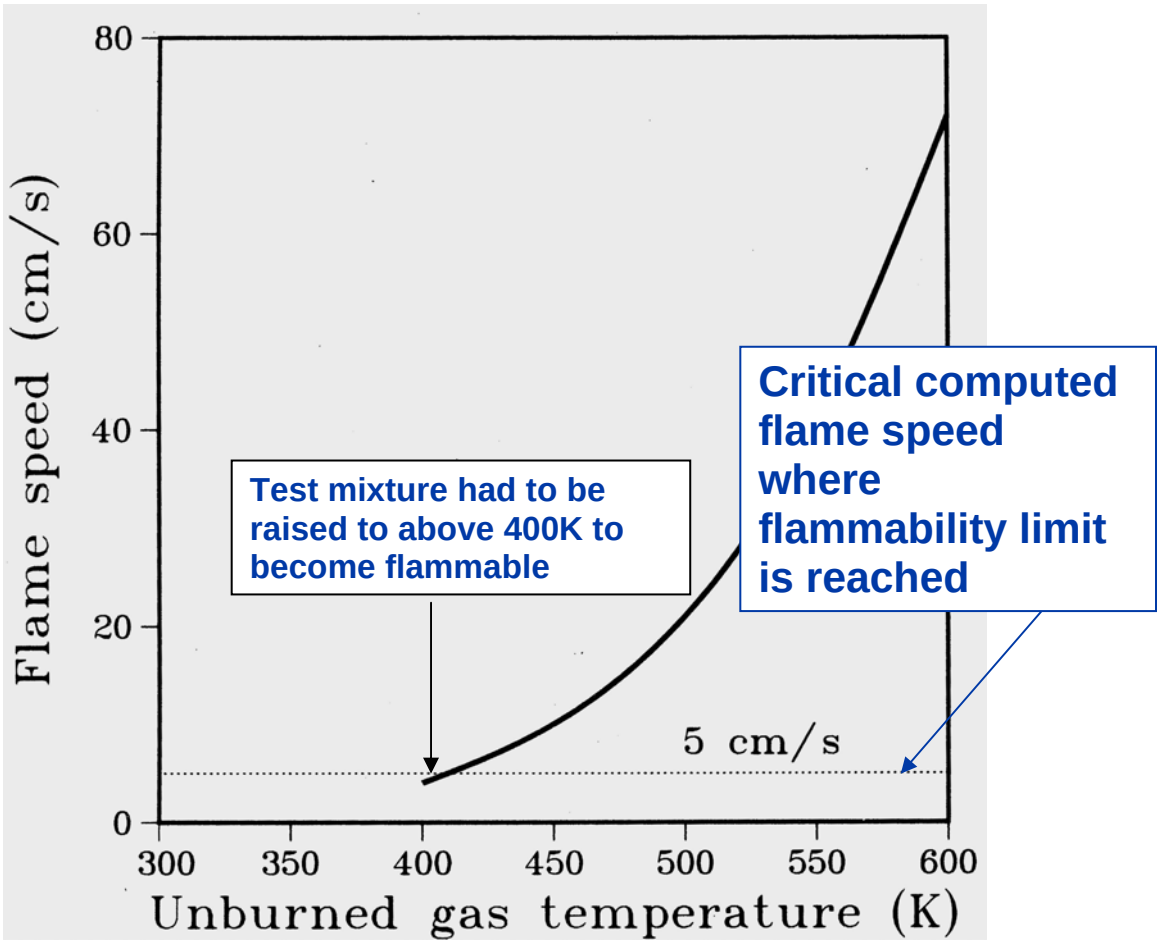

Figure 4: Computed flame speeds of a test mixture (Table 1) as the unburned gas temperature is raised.

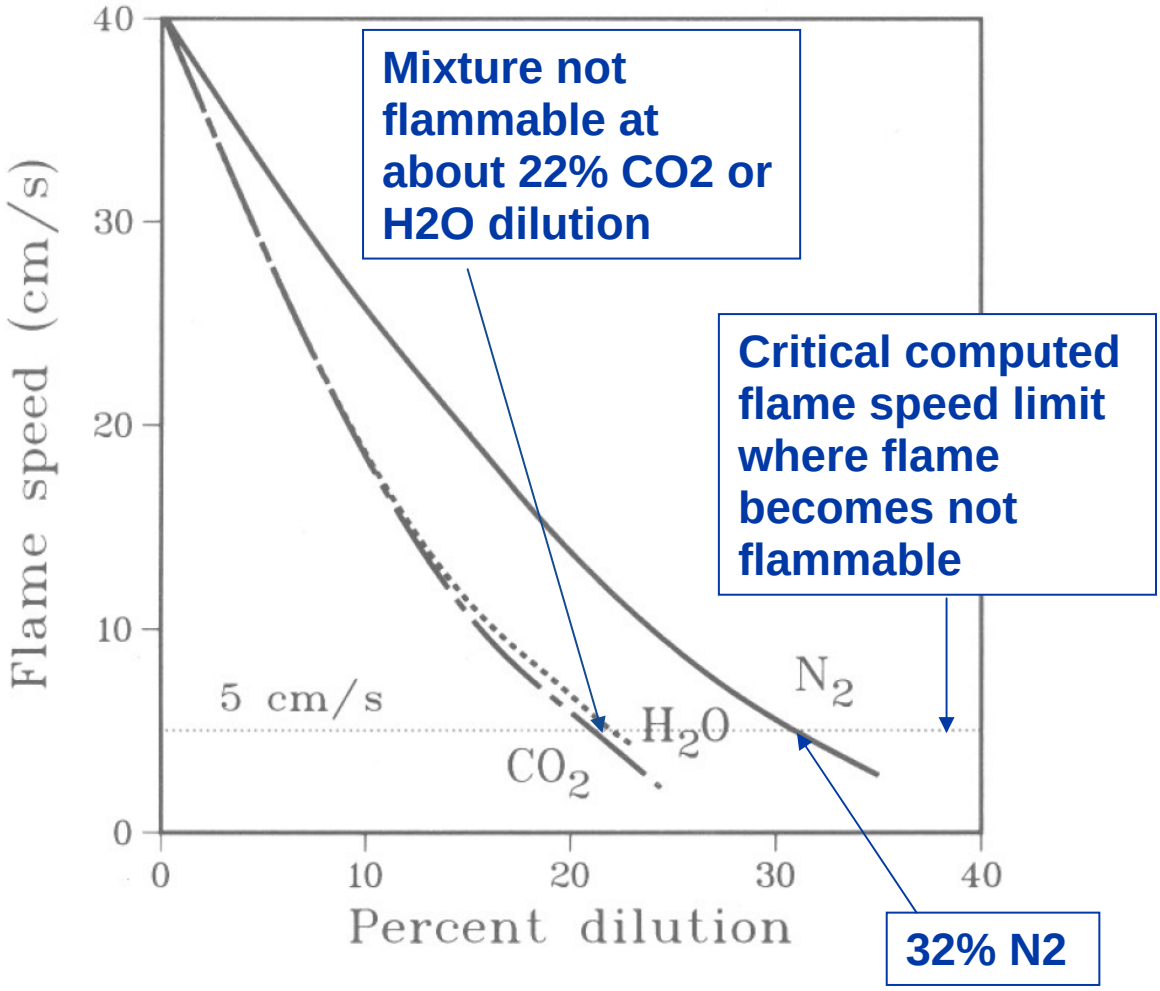

Figure 5: Computed flame speed of test mixture as different diluents are added. An "air leak" is assumed to increase the flammability of the test mixture to 40 cm/sec.

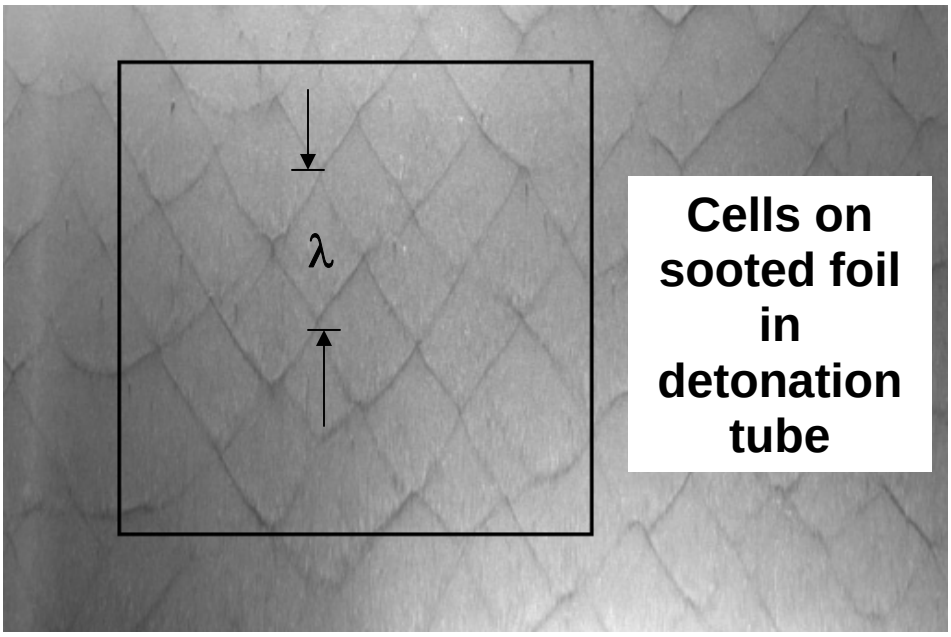

Figure 6: Cellular structure inscribed on soot foil. λ is the cell width. Photo is from [20].

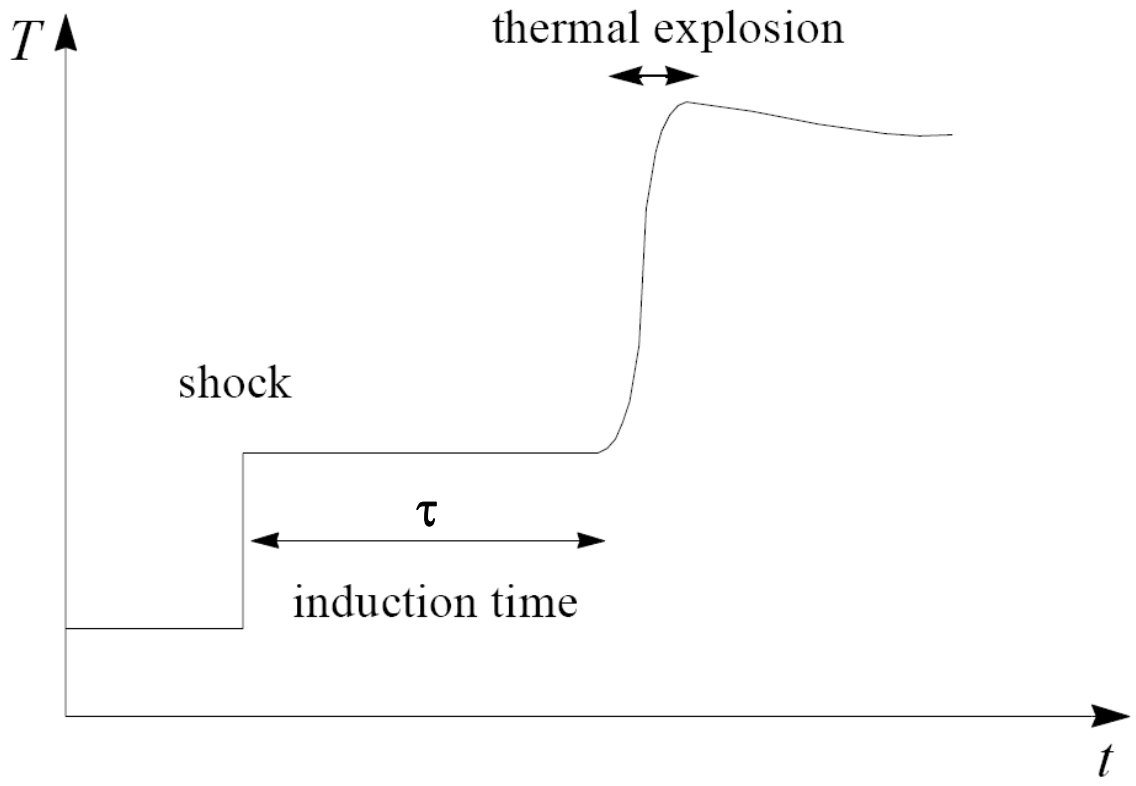

Figure 7: Induction time of reacting mixture behind a shock wave.

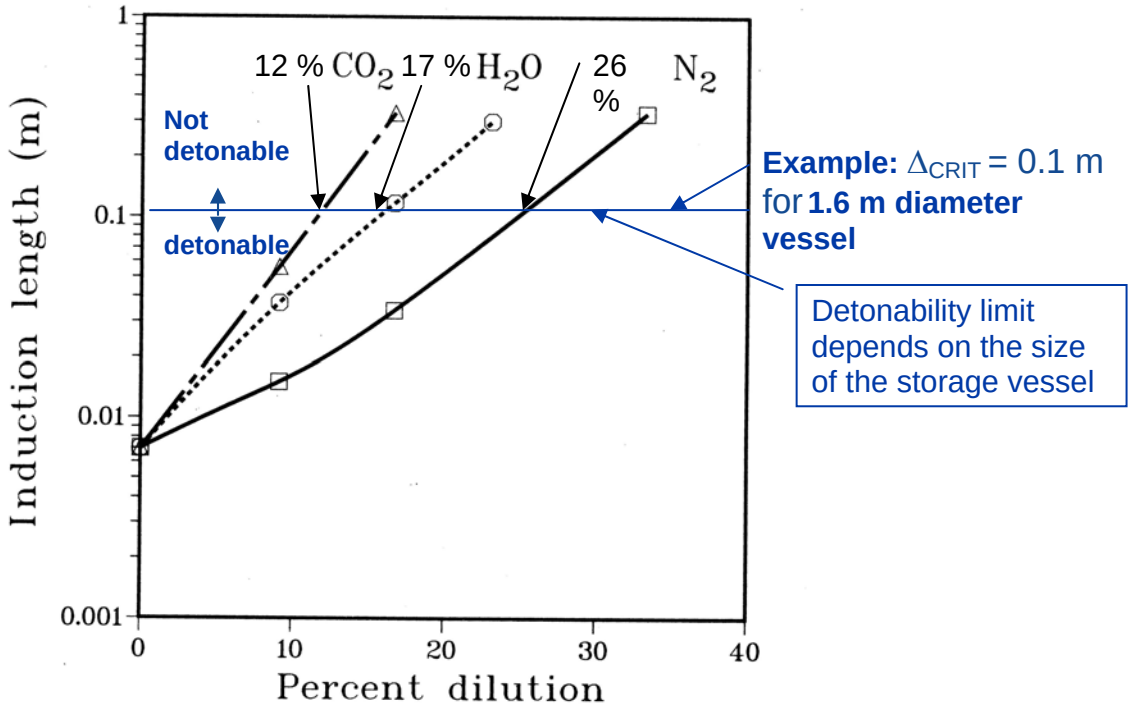

Figure 8: Induction length of a hydrogen mixture as different diluents are added, in turn. An air leak is assumed to give 10% O_2 in the test mixture and make the mixture detonable.

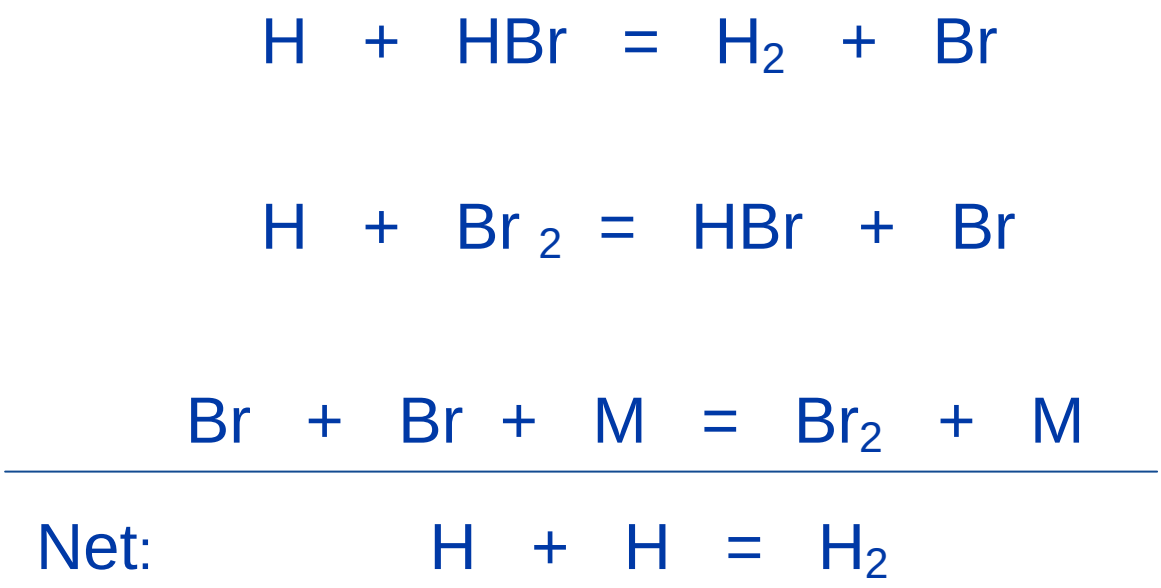

Figure 9: Catalytic cycle for bromine containing inhibitors that act by recombining H atoms in flames [7].

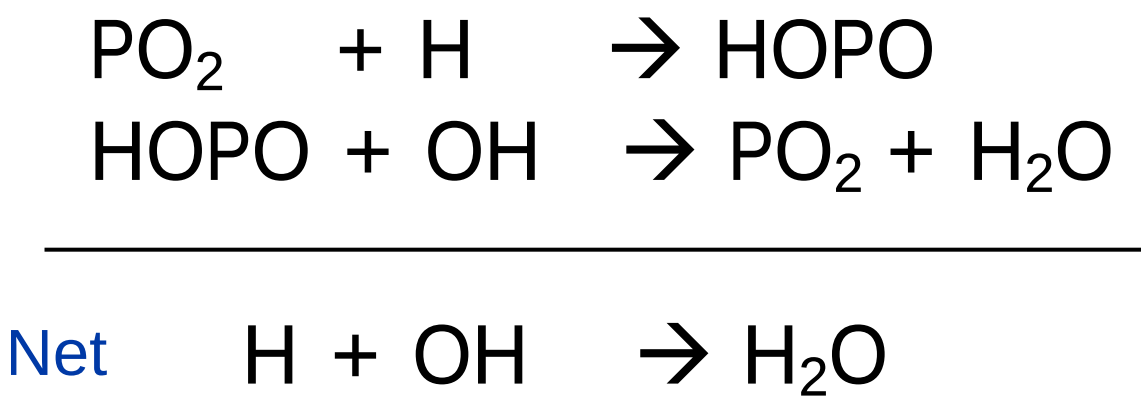

Figure 10: Catalytic cycle for recombining reactive radicals in hydrogen flames with organophosphorus inhibitors.